

CO₂ Saturations and Transport Mechanisms in Frio Sandstone [Paper 157]

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Introduction

Concern for greenhouse gases will undoubtedly increase carbon dioxide (CO₂) injection into geological formations for EOR and sequestration. The development of CO₂ plumes and subsequent dissolution into formation brine are essential mechanisms in most scenarios for sequestration. This paper describes laboratory tests on Frio sandstone core samples. Several types of displacement tests were performed; gas injection to a pseudo-residual brine saturation with respect to gas, followed by brine injection to a pseudo-residual saturation gas with respect to brine. The level of CO₂ saturation in the injected brine at reservoir pressure and temperature was varied from zero to over 90 %. This variation in CO₂ saturation in the injected brine was to determine the effect on the CO₂ saturation or plume size in the core.

What?

It was desired to determine the saturation of CO₂ that was injected into a core originally saturated with brine until no water except that vaporized into the CO₂ phase vapor was being produced. Then to follow this with the injection of brine into the core and determine when brine was displacing free CO₂ versus where only CO₂ dissolved in the brine is produced.

Why?

CO₂ is being injected into reservoirs nearing their waterflood economic limit and into aquifers, thus injecting CO₂ into geological formations containing high brine saturation. To aid in conformance control and reduce the amount of CO₂ required for injection, CO₂ and water are alternately injected into oil reservoirs. Also, it is being proposed to inject CO₂ into innumerable aquifers for carbon sequestration. Thus tests are required for both the understanding of how brine and CO₂ streams flow through porous media and how their mutual solubilities change their saturations with time.

How?

A Frio core was saturated with brine. High density CO₂ was injected into brine saturated core until brine production at a particular condition stopped. Brine was then injected into the system and CO₂ production is recorded to determine how much and when the CO₂ was produced. This procedure was repeated several times. The objective is to obtain saturation conditions and movement of brine with time and whether the brine/water was in a free phase or dissolved in the CO₂ and similarly the movement of CO₂ with time and if it is a free phase or dissolved in the brine.

Core Flooding Apparatus

The core flooding apparatus is located in a temperature-controlled air bath, with a piston pump and separator system outside the air bath, see Figure 1. The dead volume of this system (non-flow path volume) and non-core volume was minimized by reducing the number of pressure control devices, pressure transducers and valves in the system. During the analysis care was taken to capture all the water using an ambient condition separator (liquid trap) to catch the brine/water and a salt breaker (vapor trap) to capture water vapor. For a volume check the liquid and vapor traps were weighed before and after each test and in a couple cases at an intermediate point. The wet test meter was used to determine gas production at ambient conditions. Included in the gas calculations were corrections for gas displaced by brine/water in the separator.

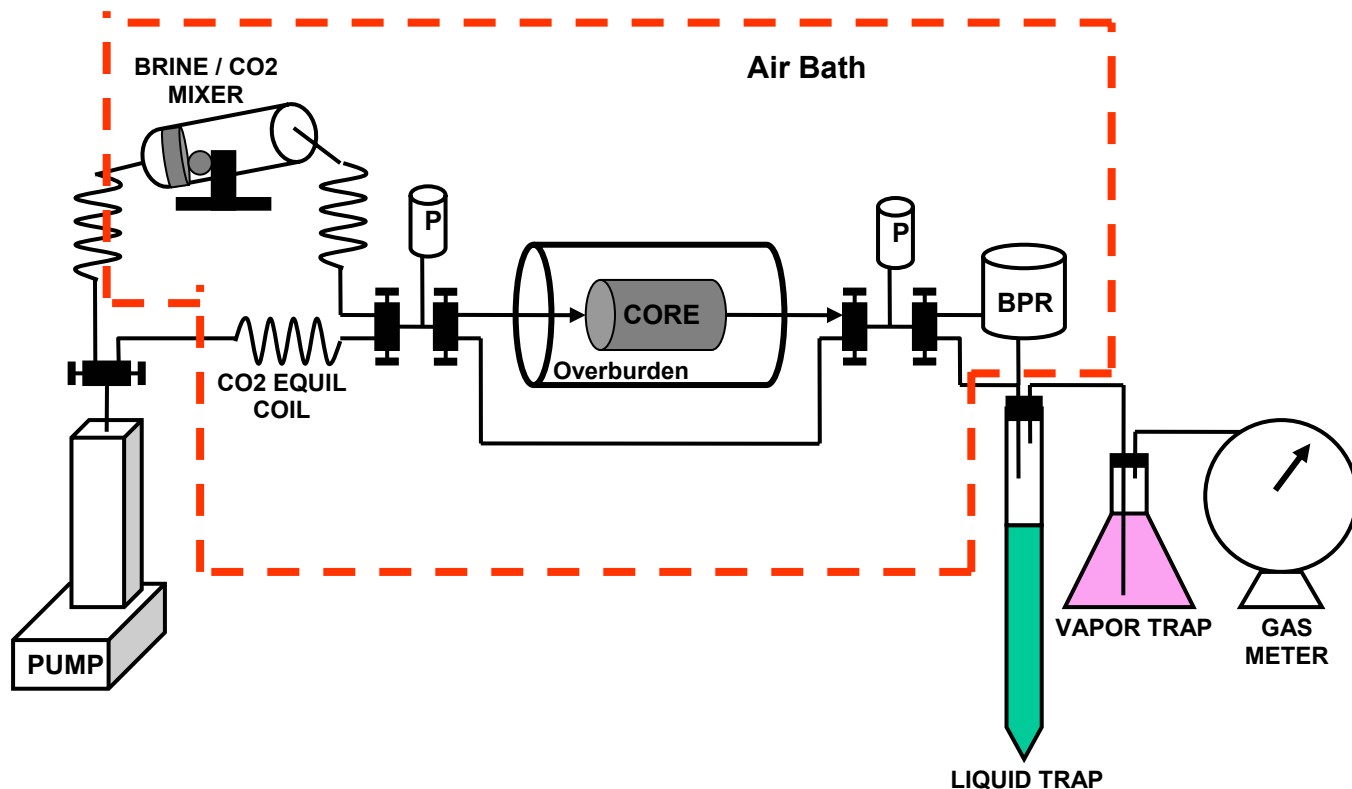


Figure 1. Schematic of the coreflood apparatus.

Material

Frio cores used in these tests were obtained from depths of 8179, 8191 and 8195 ft in the Felix Jackson # 62 Well, located in Chambers County, Texas. This is located south of the S. Liberty DOE CO₂ pilot site. These cores were selected because they were consolidated sandstone, see Frio Core Parameters listed in Table 1. The DOE carbon sequestration DOE test site south of Houston is at a shallower depth and the test horizon is in unconsolidated rock. These tests were performed in the consolidated core to minimize the difficulty while developing test procedures. Future tests if the results are found applicability will be performed on unconsolidated samples. Table 2 list the composition of the synthetic brine used in these tests and is intended to represent reservoir brine.

Table 1. Frio Core Parameters			
Core	A	B	C
Depth [ft]	8179	8191	8195
Diam [in]	1.47	1.44	1.47
Length [in]	2.393	2.4	2.25
Mass [g]	121.07	111.86	111.53
Bulk vol [cc]	66.6	64.1	62.6
PV [cc]	18.51	18.01	18.1
Por [%]	27.8	28.1	28.9

Tests Procedures

All tests were performed at reservoir conditions of 145°F and 2200 psig, except for a couple of comparison tests at 100°F (these will be indicated). The overburden pressure was maintained at 4000 psi (always a minimum of 1000 psi above the pore pressure). The brine was prepared with the composition indicated in Table 2. In some cases the brine had CO₂ dissolved in it to represent brine that had been in contact with CO₂. The brine will

Table 2. Frio Synthetic Brine Composition			
Component	mg/L	Species	mg/L
NaCl	82,753	Cl	57,460
CaCl ₂	8,584	Na	32,603
MgCl ₂	2,152	Ca	3,100
KCl	362	Mg	549
NaHCO ₃	186	K	190
		HCO ₃	135
Total Dissolved Solids	94,037		94,037

be indicated as Dead-Brine (no dissolved CO₂), 50% CO₂-Brine (brine saturated to about 50% CO₂), and 90% CO₂-Brine (brine saturated to about 90% CO₂). Brine saturated to 100% CO₂ was not used to insure no new free CO₂ would occur from CO₂ evolving out of the brine. Pressure drop across the core and dissolved solid changes in the brine due to dissolution of core material or water vaporizing into the CO₂ phase could cause additional CO₂ phase to occur if brine 100% saturated with CO₂ was injected. In all but one case the coreflood was initially 100% saturated with Dead-Brine. Dehydrated CO₂ was then injected into the core at least until no free brine was being produced for several pore volumes. CO₂ was stored outside the air bath at ambient temperature and injected at rates from 10 to 200 cc/hr (20 cc/hr was used unless otherwise indicated) at ambient temperature and about 2200 psig. The CO₂ injection volume at 145°F was about 65% higher than at ambient temperature; both at 2200 psig. The temperature of the air bath, core, and injection pump were recorded. The head and end volumes of the core system were 4.3 cc, thus in Figures 2, 3 and 8 through 10 the volumes are shown starting at -4.3 cc.

Discussion of Results

Figure 2 compares two tests of CO₂ displacing brine in Frio Core A. In both about 7 cc of brine was produced before CO₂ breakthrough. After CO₂ breakthrough there was a small quantity of brine produced and then brine production stopped except for water dissolved in the CO₂. Normally over 95% of the brine production occurred before 1 pore volume (PV) of CO₂ had been injected. Any continued production after about 1 PV of CO₂ had been injected was from vaporized water. At the end of the test the salt vapor trap was weighed and this value added evenly over the duration of the test versus injection rate to the brine/water production weight determinations. The time when the vapor was actually produced is not known. In Figure 2 the first system had an injection rate increase from 20 to 100 cc/hr after 200 cc of CO₂ had been injected. Note the increase in the rate of brine production for an interval following the injection rate increase. During the second test injection was continued over night at a reduced injection rate of 10 cc/hr and then increased to 100 cc/hr for a short time period at the end of the test.

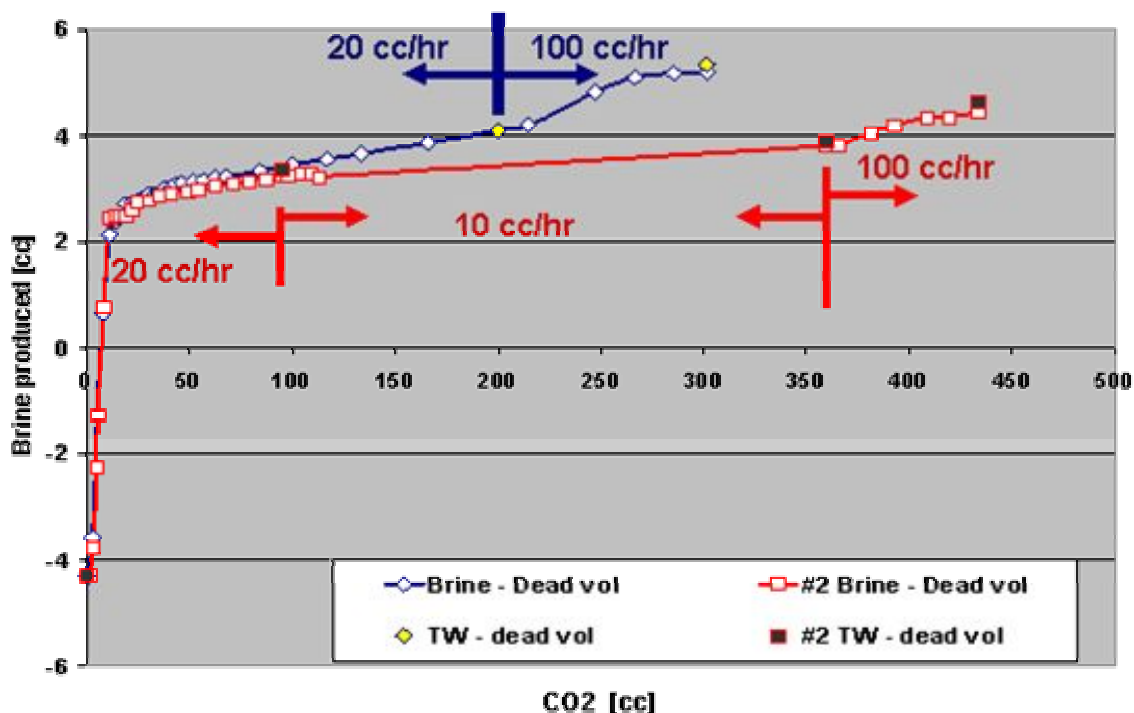


Figure 2. Comparison of brine production during CO₂ injection of two tests both in Frio Core A. In each the 4.3 cc dead volume is subtracted. The points were the volumes by weight were determined are indicated for each as TW and compare well with the values determined by direct volume with the vapor trap values included.

In each case after reaching what might be considered a pseudo-end point. Stable saturation can be changed by increasing the flow rate, decreasing pressure, or by evaporating brine saturation, thus there is no true end point.

For this paper it will be referred to as a pseudo-end point. After completion of CO₂ injection, brine was injected into the core to displace the CO₂. For both tests shown in Figure 2, Dead-Brine was injected, see Figure 3. It is interesting that when about 4.3 cc of reservoir condition CO₂ was produced (the same as the end plate dead volume) the CO₂ production rate decreased significantly. After the production decrease, an additional 5 cc of CO₂ at reservoir condition were produced at a constant rate. Using values from Wiebe and Gaddy (1940) adjusted for dissolved solid (Enick 1990), these rates are what would be expected from CO₂ dissolved in Frio Brine at the test conditions. The produced CO₂ after the dead volume was produced did not advance as a free phase. The final value of produced CO₂ from the system including blow down to ambient pressure was equal to the brine produced during CO₂ injection, thus a good material balance was obtained.

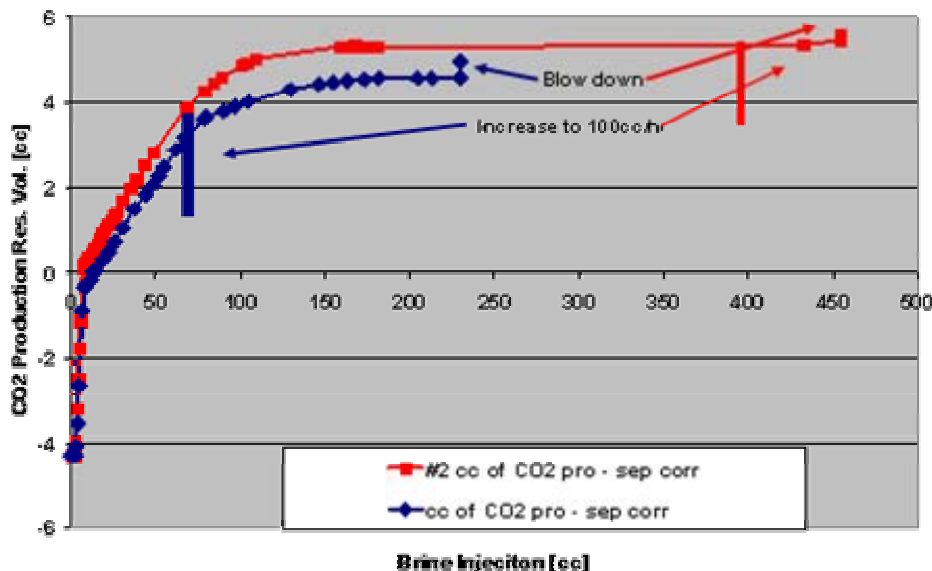


Figure 3. Comparison of CO₂ production during brine injection for two tests in Frio Core A. In each the 4.3 cc dead volume is subtracted.

The second set of experiments was performed using Frio Core B. In this set the test procedure was similar to that used for Frio Core A, except that the CO₂ concentration in the injected brine was varied from 0 to 90% of full saturation. Figure 4 shows the production rate of CO₂ in cc/min at ambient conditions for three brines tested at a production flow rate of 20 cc/hr. Thus these values multiplied by three would be the dissolved CO₂ in a cc of brine at reservoir conditions. Figure 5 compares the production rate of CO₂ while injecting brine into Frio Core B during three different tests. Excluded in Figures 5 through 7 was the CO₂ production rate during the early brine injection period where the production of the CO₂ phase was occurring. See the example in Figure 9 where the early CO₂ production rate is included in the plot. In all cases the rate of CO₂ phase production is in the 100 to 200 cc/min range with a brine injection rate at 20 cc/hr. Of the three tests shown in Figure 5, each one followed the injection of CO₂ into the core saturated with Dead-Brine. The three tests differ in the concentration of CO₂ in the injected brine. During the early time period of dissolved CO₂ production (see Figure 6) the production rates are essentially equal for all three scenarios. The brine produced from this 2.4 inch core was saturated with CO₂ and did not depend on the CO₂ concentration of the injected brine. Thus the brine was saturated with CO₂ in a relatively short flow path. Also shown for comparison in Figure 6 is the production rate of 50% CO₂-Brine and 90% CO₂-Brine.

The injection test using 90% CO₂-Brine was not continued until free CO₂ was depleted in the core as in the other two cases. Injection and production continued long enough to verify the production rate of CO₂ during the first part of the injection. From Figure 5, CO₂ depletion in the core during the Dead-Brine injection shows a rapid decline in the CO₂ production rate after most of the CO₂ had been produced. In the 50% CO₂-Brine the drop is slower and as might be expected the system stabilizes at a rate of about 3 cc/min which is the same as the content of the brine being injected, see Figures 4 and 6. When the pressure was lowered to ambient pressure (blow down)

at the end of the 50% CO₂-Brine test, the produced CO₂ was equal to what would be evolved from 1 PV of brine saturated to 50% CO₂, indicating that all the free CO₂ had been removed.

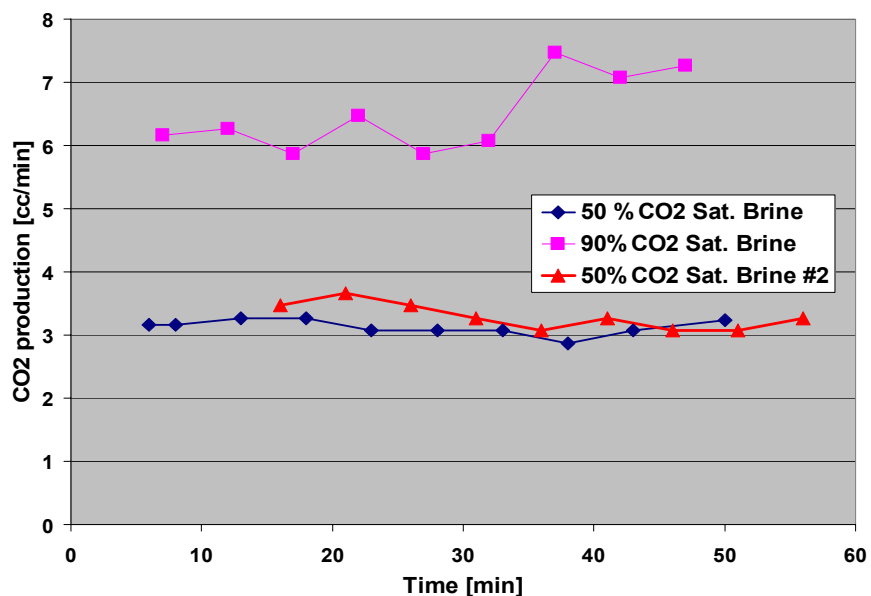


Figure 4. Comparison of CO₂ production (cc/min) from two brines saturated to about 50% CO₂ and one saturated to 90% CO₂; each at a flow rate of 20 cc/hr and 145°F.

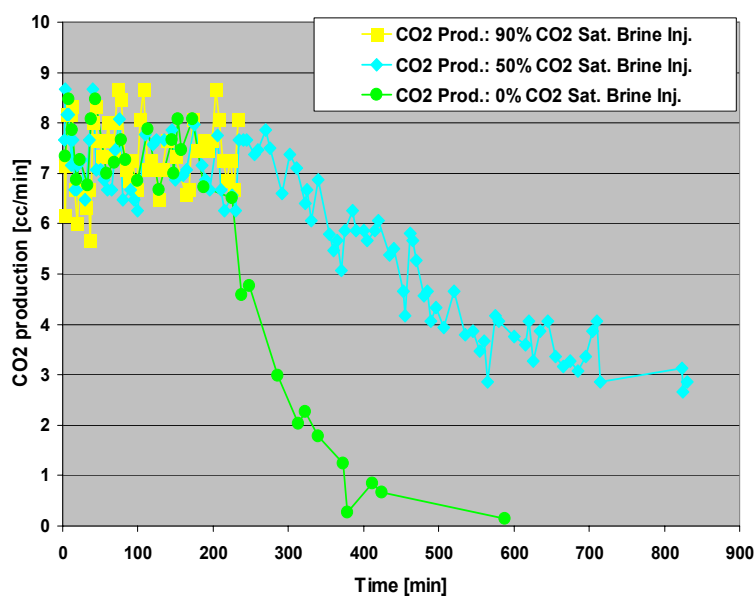


Figure 5. Production rate of CO₂ during the injection of brine into Frio Core B for three different tests, each at different concentrations of CO₂ in the injected brine.

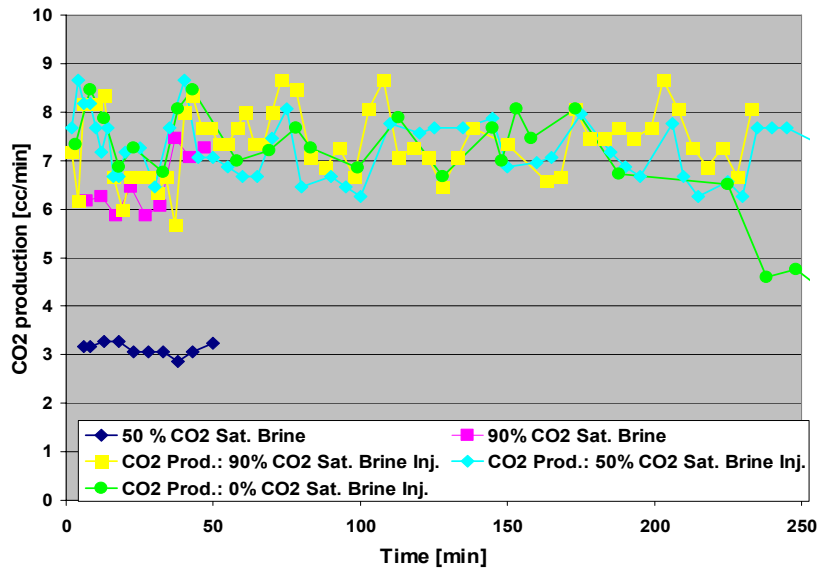


Figure 6. Comparison of CO₂ production rates during brine injection into Frio Core B during from about 1 PV to 5 PV.

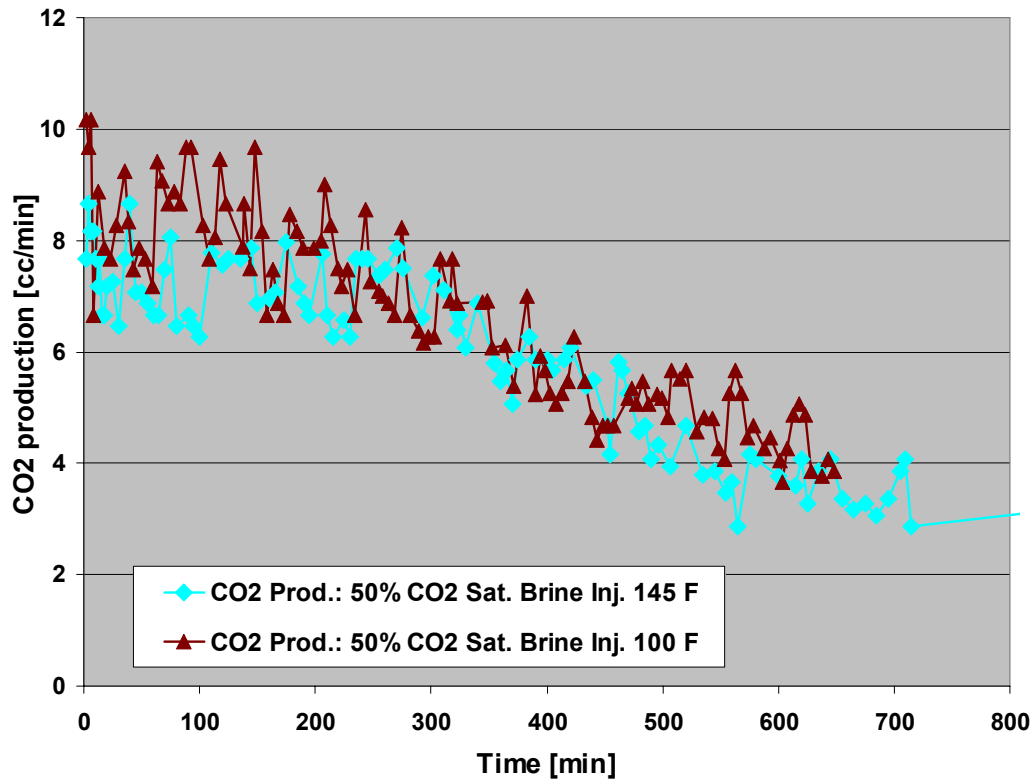


Figure 7. Comparison of the CO₂ production rate during the injection of 50% CO₂-Brine at two different temperatures, 100° and 145°F.

Figure 7 compares the production of CO₂ during the injection of 50% CO₂-Brine at two temperatures, 100° and 145°F. The production rates are similar but it appears that the CO₂ production rate is a little higher at 100°F. Literature values (Weibe and Gaddy, 1040) indicate that the solubility of CO₂ in brine is around 10-15% higher at

the lower temperature. Even though the data has scatter similar to the expected difference, the average for the first 200 minutes in Figure 7 is 7.3 cc/min at 145°F and 8.3 cc/min at 100°F which is a 14% increase in production at the lower temperature.

The results of the final set of tests reported in this paper were from Frio Core C, see Figures 8 through 10. Figure 9 has an expanded production rate scale compared to Figure 8 to demonstrate the rate comparison during free CO₂ production and production evolving from CO₂ dissolved in brine at reservoir conditions. In this series the first tests performed started with a dry core. The core was then saturated with 100% dehydrated CO₂ and followed with the injection of Dead-Brine into the core. In this system about 9 cc of CO₂ at reservoir conditions were produced before production stabilized at the rate evolved from brine saturated with CO₂ at 100°F and 2200 psig. About 11 cc of CO₂ at reservoir conditions were produced at a rate of about 8 cc/min at ambient conditions, thus a total of about 20 cc at reservoir conditions. From this subtract the 4.3 cc dead volumes, thus leaving 16 cc or almost 90% of the 18.1 cc core PV. Another 2 cc were produced during the remaining injection period and blow down after injection was terminated. In this test it required about 4 cc of brine or just over 0.2 PV to establish a brine flow path. At or soon after a brine flow path (brine breakthrough) is established CO₂ phase production ended. Shortly after brine breakthrough it appears that only CO₂ dissolved in produced brine was produced.

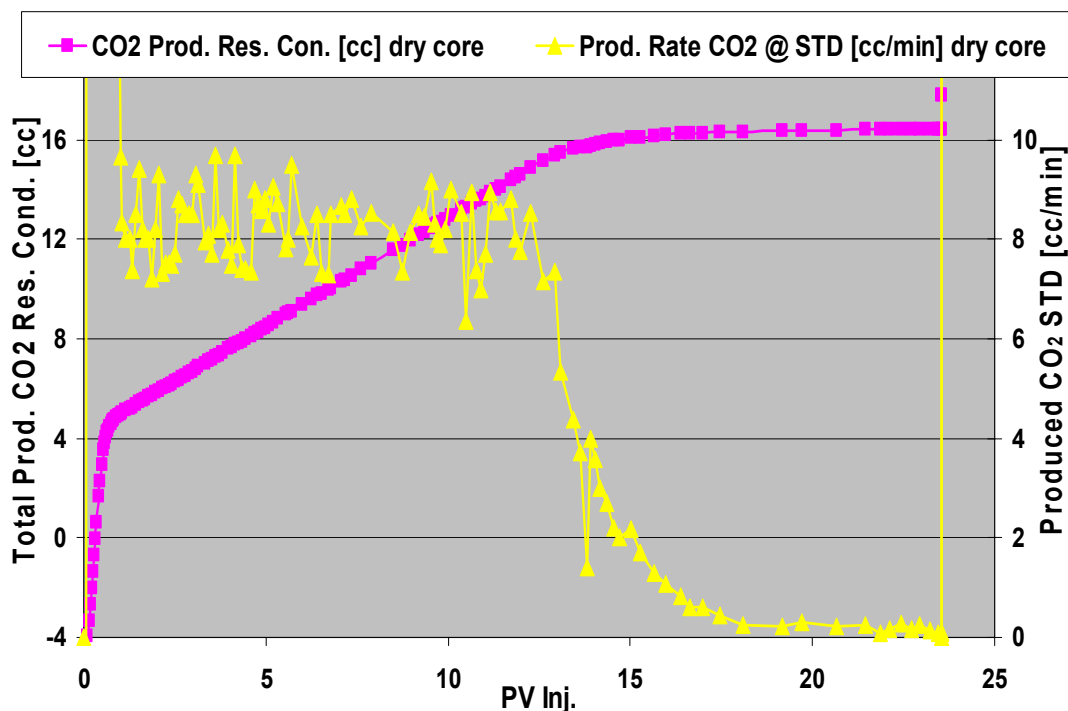


Figure 8. Comparison of total CO₂ production at reservoir conditions and production rate from the separator at ambient conditions for CO₂ during the test at 100°F.

After the pressure of Frio Core C was reduced to ambient pressure Dead-Brine was injected to remove any remaining CO₂. To compare to Frio Cores A and B the system was returned to reservoir pressure, but left at 100°F. Again the dead volume and a few cc of additional brine were produced. When the production of free brine stopped 50% CO₂-Brine was injected. Figure 10 compares the production rate and total production of CO₂ during the injection of the 50% CO₂-Brine with the injection of Dead-Brine into the dry CO₂ core. The results are different from Frio Cores A and B, in that CO₂ phase production terminated before the dead volume equivalence of CO₂ was produced. This had occurred once before and in both cases it appeared that brine had remained in the end plates of the core and/or in the lines and thus not as much brine injection was required to push out all the CO₂ phase. In one case, after CO₂ injection into the core ended and the lines isolated from the core about 1 cc of brine was blown out of the lines. In all the other tests the system lines had been brine/water free. The slope of the cumulative production for the second tests is about half that of the first tests because the CO₂ dissolved in the 50%

CO₂-Brine that was being injected was subtracted from the produced CO₂ when calculating the CO₂ production during brine injection.

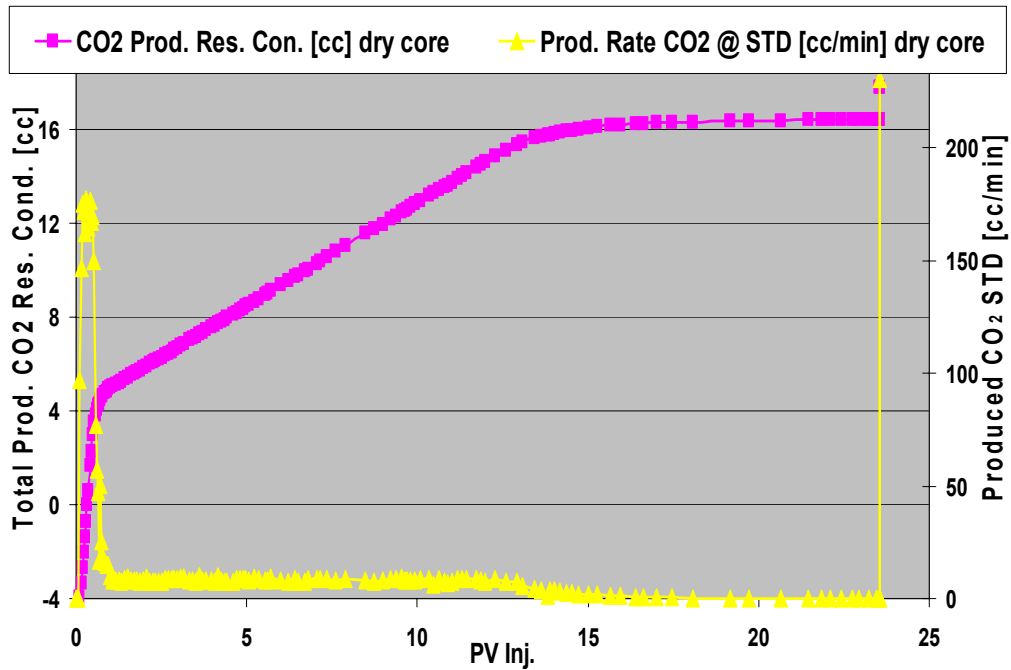


Figure 9. Comparison similar to Figure 8 except the scale for CO₂ production rate is expanded to include the maximum production rate during production of the CO₂ phase.

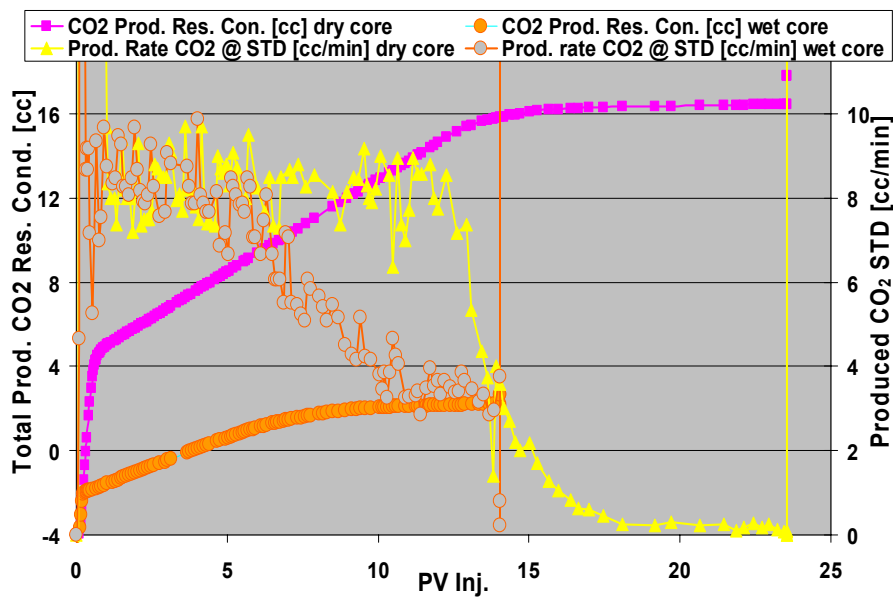


Figure 10. Comparison of CO₂ production of brine into the dry Frio Core A and injection of 50% CO₂-Brine into the core after being saturated with Dead-Brine and then flooded with CO₂.

Summary and Conclusions

These were relatively short cores (2.25 to 2.4 inches) about 1.5 inches in diameter, therefore care must be taken when extrapolating results to reservoir scale. Some of the conclusions are:

1. In the range of 0.2 to 0.3 PV fraction of CO₂ phase saturation was required to establish a CO₂ flow path after which there was little brine production except through evaporation. CO₂ saturation can be increased by increasing flow rate, reducing pressure, and water evaporation.
2. At the end of CO₂ injection there was a relatively low CO₂ saturation and high brine saturation in the core, and no apparent reduction in CO₂ saturation was required to return to establish brine flow path. In the case of a water wet systems this and the previous conclusion are not surprising.
3. Brine is equilibrated with CO₂ in minutes over a relatively short distance.
4. In the systems tested, once CO₂ injection stopped, the CO₂ phase did not migrate and did not change except to the extent that unsaturated brine was available to dissolve CO₂.
5. The injection of brine into a 100% CO₂ phase required less then 0.3 PV fraction saturation to establish a brine flow path.

This is an ongoing work. We are presently looking at carbonate core and for each core type determining pore body and throat size distributions.

Acknowledgements

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